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DISTRIBUTION AND RELATIONSHIPS OF HEAVY METALS IN THE GIANT CLAM (*TRIDACNA MAXIMA*) ANDASSOCIATED SEDIMENTS FROM DIFFERENT SITES IN THE EGYPTIAN RED SEA COAST

HASHEM ABBAS MADKOUR

Marine Geology Researcher (Ph.D), National Institute of Oceanography and Fisheries, Hurghada Research Station, Red Sea Branch.

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ABSTRACT

The giant clam (*Tridacna maxima*) and sediments have been collected from clean and contaminated coastal sites of the Egyptian Red Sea. Selected samples of the giant clam shells and the associated surface sediments were analyzed for Fe, Mn, Zn, Cu, Pb, Ni and Cd. Significant spatial differences in metal concentrations in *Tridacna maxima* and sediments were identified. Copper and lead are greatly enriched in the giant clam shells, which is related to their physiological function. Cd content is higher in *Tridacna maxima* than in sediments, because of the easy substitution between Cd and Ca. The levels of most metals in the giant clam shells and sediments were higher in the anthropogenic sites than in the uncontaminated sites. Generally, metal variations reflect natural conditions and human activity. Moreover, there are no clear relationships between concentrations of heavy metals in the giant clam shells and those in sediments.

INTRODUCTION

Marine organisms, including molluscan shells, accumulate contaminants from the environment and therefore have been extensively used in marine pollution monitoring programs. Bivalves have been shown to be valuable sentinel organisms (Farrington *et al.,* 1982 & 1983) because they greatly concentrate many chemical elements from seawater and sediment, making analysis easier. At the same time they integrate pollutant levels over time, thereby giving a more realistic indication of the pollution status of the environment (Huanxin *et al.,* 2000). Knowledge of concentration factors of metals in marine organisms is useful for recognizing the relative ability of organisms to bioaccumulate selected metals from their environment (Szefer *et al.,* 1999). The mollusc shells consist of three different layers. The outer layer is usually chitinous (periostracum), the middle layer is formed of CaCo3 and the inner layer is calcareous (nacreous layer). The outer layer, which covers the whole surface of the shell, is organic and has a protein base (Milliman, 1974). The shells increase flexibility needed in environmental stresses (Wainwright, 1969) and start out as a single homogenous layer. The remainder of the shell is formed mainly of calcium carbonate. In addition, Simkiss (1983) suggested that concentrations of trace elements in shells provides a series of natural probes for calcification systems, and their study could provide fundamental information on the processes involved. The possible use of bivalve's molluscs as indicators of trace metals in ambient water has also received considerable attention.

Recent studies have recommended continuous chemical and biological investigations on marine environments to assess anthropogenic impacts and

E-mail: Madkour_Hashem@yahoo.com

remediation (Mansour *et al.,* 2005). Published informations on the levels of heavy metals in mollusc shells of the Egyptian Red Sea coast (Ziko *et al.,* 2001; Madkour, 2004 and Mansour *et al.,* 2005) are insufficient.

The present study focuses on areas subjected to natural impact from wadis such as Hamata Reefs, Abu-Ghusun Lagoon and Wadi El-Gemal area; and anthropogenic activities which included Quseir, Safaga, Hurghada Harbors and El-Esh area (Fig. 1). Anthropogenic activities in these areas include shipment of ores such as phosphate and bauxite, coal and cement packing, renewing ship operations, and shipyards, landfilling, dredging and oil production especially in Hurghada Harbor and El-Esh area.

The two valves of *Tridacna maxima* Röding 1798 (Fig. 2) can exceed 8 inch (20cm) in length (Wye, 1991). The giant clam lives firmly attached by its byssus to coral in the mid-reef section. It is a locally common large shell in shallow reefs to about 15m. This species is widely distributed in the Red Sea, Arabian Sea and Indo-Pacific province. It is abundant in the south areas especially in Hamata reefs but rare to frequent in the human activity sites. It is a valuable seafood source and indiscriminately overfished, so collection of this species is now monitored.

The giant clam (*Tridacna maxima*) lives near the sediment-water interface; therefore, contaminants and heavy metals in sediments have potential influence upon. The purpose of the present study is to understand the relationship between *Tridacna maxima* and sediment, by measuring heavy metals Fe, Mn, Zn, Cu, Pb, Ni and Cd in the shells of giant clam (*Tridacna maxima*) and sediments collected from different sites of the Red Sea coast.

MATERIALS AND METHODS

Sediments and shells of the giant clam (*Tridacna maxima*) were sampled from seven sites along the Egyptian Red Sea coast during 2004. The locations of sites and their positions are show in (Fig. 1) and (Table 1). Using SCUBA diving the giant clam and sediments were collected from the study sites. The giant clam shells were cleaned and the soft tissue was removed on the beach of the sampling site. Oceanographic parameters such as salinity, temperature, pH and dissolved oxygen were determined in a water sample overlying each sampling site. Temperature, salinity, dissolved oxygen (DO), pH, total dissolved salts (TDS), oxidation reduction potential (Eh) and specific conductivity (SPC) were measured at different depths of the studied localities using the Hydrolab Instrument (Surveyor $^{(4)}$ 1997) as shown in (Table 1).

The empty shells were soaked in water for 15 – 30 minutes in order to kill any clinging algae then left to dry in air. The sediment samples were gently washed several times by distilled water to remove soluble salts, then spread on glass sheets and left to dry in air. About ten grams of shell parts and sediments were ground to a powder using an agate mortar (Retsch Mortar), passed through a 80 mesh sieve and kept in dry, clean bag waiting for analysis. 0.5 gram of the prepared ground sample was completely digested in a Teflon cup by using a mixture of conc. Nitric (HNO3), perchloric (HClO4) and hydrofluoric acids (HF) with the ratio 3 : 2 : 1 respectively according to (Oregioni and Aston, 1984). Acids were slowly added to the dried sample and left overnight before heating. Samples were heated at temperature of approximately 200^{o}C, then left to cool and filtered to get rid of the nondigested parts.

The solution was justified to a volume of 25ml, then the concentration of elements were determined by AAS (Atomic Absorption Spectrophotometery) technique, using GBC–932 ver. 1.1 of the National Institute of Oceanography and Fisheries, Hurghada. Results were expressed in ppm.

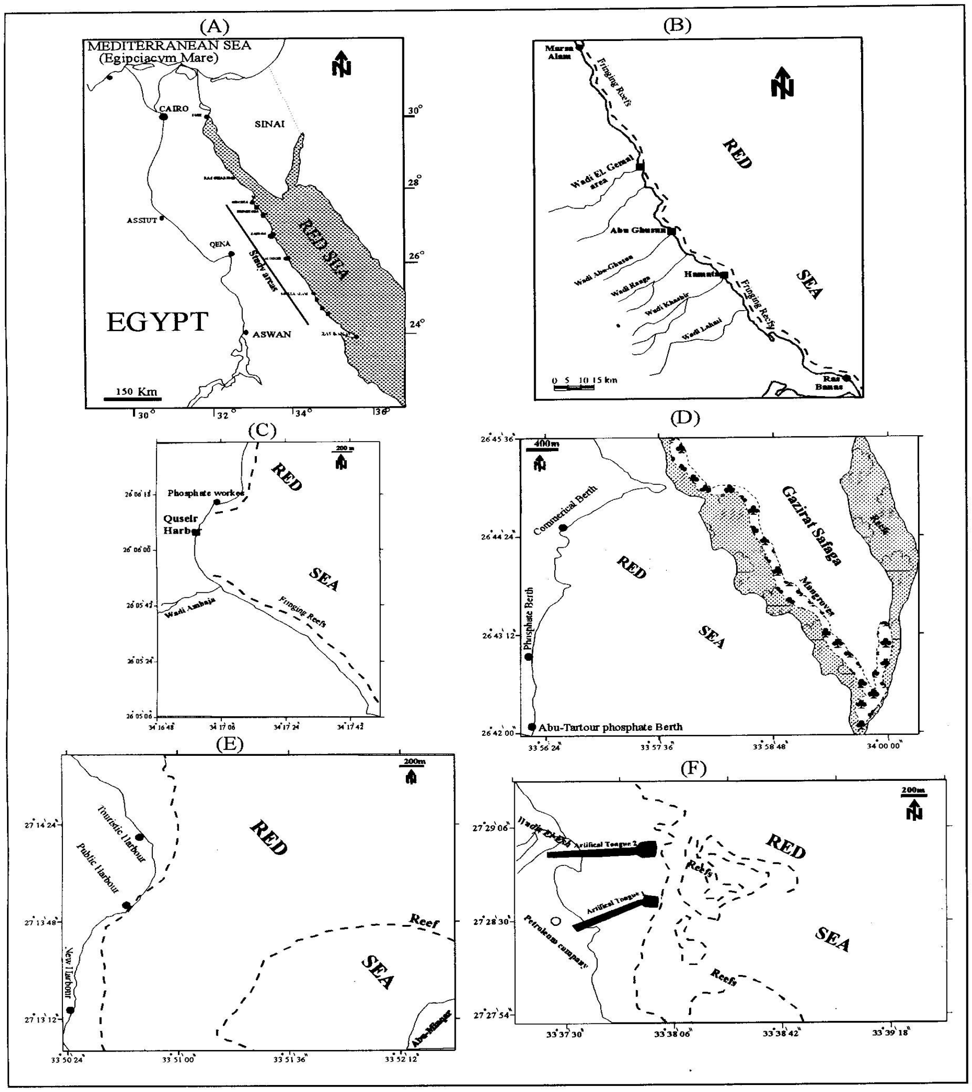

Fig. (1). Location maps, general view of the Red Sea (A), Hamata, Abu Ghusun and Wadi El-Gemal areas (B), Quseir Harbor (C), Safaga Harbor (D), Hurghada Harbor (E) and El-Esh area (F).

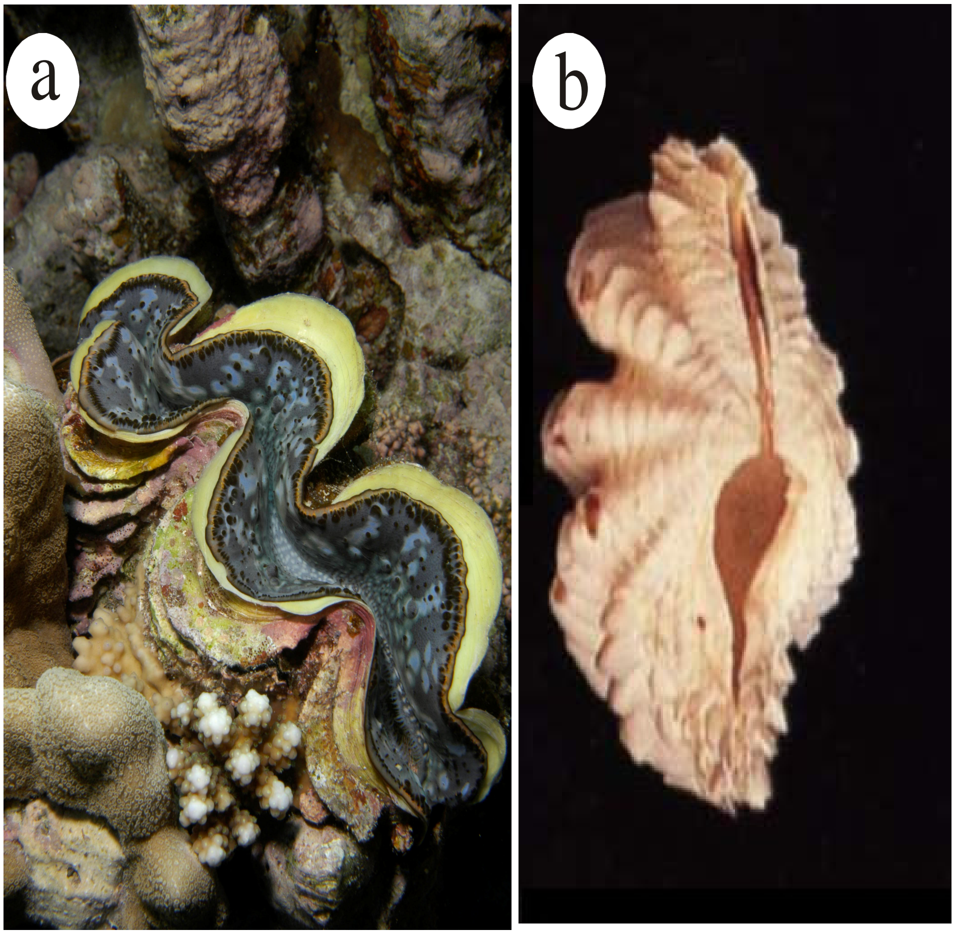

Fig. (2). *Tridacna maxima*, underwater photograph showing general view (a),the hinge line of the giant clam 0.4X (b).

RESULTS AND DISCUSSION

Concentration of heavy metals

The results obtained from the analysis of the giant clam shells and sediments from the studied localities are shown in (Table 2).

Iron and Manganese

Iron concentration in *Tridacna maxima* varies from 216.4ppm at Abu-Ghusun Lagoon to 1286.4ppm at Safaga Harbor. While in the sediments it ranges from 768.7ppm at Hamata reefs to 9546.3ppm at Safaga Harbor (Fig. 3a). This means that the concentration of Fe in sediments is 6.6 times that in *Tridacna maxima*. Generally, anthropogenic sites recorded high values of Fe in sediments and the shells of *Tridacna maxima* compared with those of the natural impact sites. Iron plays an important role as an essential element in all living systems from invertebrates to humans but increasing of iron in the marine environment may reflect the bioaccumulation in the marine organisms such as, bivalves, gastropods, coral reefs and fish. Ramadan and Shata (1993) stated that the concentration of iron in the bivalve's shells depends to some extent, on the iron concentration in food supply and on the organism's growth rate.

Mn content in the giant clam shells ranges from 29.9ppm at Abu-Ghusun Lagoon to 65.2ppm at Safaga Harbor. In sediments, it ranges from 42.3ppm at Hamata reefs to 1245.4ppm at Safaga Harbor. This means that the concentration of Mn in the marine sediments is 11 times that of the giant clam shells. Similar to Fe, anthropogenic sites have the higher Mn values compared with the natural sites (Fig. 3a).

Obviously, the marine sediments and *Tridacna maxima* in Safaga and Quseir Harbors have the highest values of Fe and Mn compared with the other studied localities. This is may reflect different shipment activities such as phosphate shipment; bauxite and cement packing, especially in Safaga Harbor and renewing ship operations.

Zinc and Copper

The highest concentration of Zn in *Tridacna Maxima*, is recorded in Hurghada Harbor (32.6ppm), while the lowest one in Quseir Harbor (11.4ppm). On the other hand, the highest value of Zn in marine sediments is recorded in Wadi El-Gemal area (74.6ppm), while the lowest one in Hamata reefs (23.7ppm). This means that the concentration of Zn in the marine sediments is 1.4 times higher than of *Tridacna maxima* (Fig. 3a). On the other hand, *Tridacna maxima* recorded high values of Zn in Hamata reefs and Abu-Ghusun Lagoon compared to the marine sediments. Mansour *et al.,* (2005) reported that zinc is mainly co-precipitated with calcium carbonate and substitute calcium to form isomorphous zinc carbonate. The uncontaminated sites recorded higher values of Zn compared to the human impact sites. This is probably due to the influence of terrigenous sediments to the marine environment. Moreover, in Harbors, usually huge amount of chemical materials (e.g., zinc sulphate) is used for the marine painting processes, usually zinc sulphate are widely distributed along the coast of Hurghada Harbor.

Copper is an essential and potentially toxic element (Merian, 1991). The Cu content in the giant clam shells ranges from 12.4ppm at Hurghada Harbor to 81.4ppm at Abu-Ghusun Lagoon. These contents are comparable to those of the marine sediments where Cu ranges from 8.7ppm at Quseir Harbor to 82.7ppm at El-Esh area (Fig. 3a). On the average, the concentration of Cu in *Tridacna maxima* at the studied localities is only 1.2 times higher than in sediments. Moreover, the natural sites recorded high values of Cu content in *Tridacna maxima* and sediments compared to the human impact sites except in El-Esh area. This is probably due to the influence of terrigenous flux by wadis derived from the nearby volcanic and ultramafic rocks.

Table (1). Sample location, depth and the measured hydrographic parameters of water mass in the studied areas.

No.	Location	Position		Depth	Temp.	Salinity	DO	pH	ORP	TDS	SPC
		Lat. o / // N	Long. o / // E	(m)	^{o}C	o\oo	mg\L		(Eh)	g\L	ms\cm
1	Hamata Reefs (HR)	24 22 41	35 15 51	4	29.74	40.85	6.73	8.29	283	38.95	60.94
2	Abu-Ghusun Lagoon (Gh)	24 27 50	35 11 37	10	23.23	41	7.71	8.57	278	39.07	61.02
3	Wadi El-Gemal (WG)	24 40 13	35 05 30	6	24.6	41.16	8.62	8.46	339	39.21	61.22
4	Quseir Harbor (QH)	26 05 01	34 17 05	3	25	40.6	6.9	8.7	375	39.3	61
5	Safaga Harbor (SH)	26 43 46	33 59 53	7	26	41.4	6.5	8.3	397	39.6	61.6
6	Hurghada Harbor (HH)	27 13 01	33 51 13	8	28	41.7	5.8	8.7	388	39.9	62.3
7	El-Esh area (Eh)	27 28 63	33 38 70	5	22	42.3	6.7	8.6	437	40.7	62.4

Table (2). The results of geochemical analysis of *Tridacna maxima* and sediments at the studied areas.

Location	samples	Heavy metals						
		Fe*	Mn*	Zn*	Cu*	Pb*	Ni*	Cd*
HR	*Tridacna maxima*	233.5	37.18	27.77	51.28	34.46	46.36	1.32
	sediment	768.69	42.31	23.68	18.96	30.11	36.42	1.24
Gh	*Tridacna maxima*	216.41	29.93	30.66	81.42	35.83	44.81	1.44
	sediment	888.41	74.34	26.91	56.21	26.17	26.21	1.22
WG	*Tridacna maxima*	564.36	30.29	31.13	51.45	33.45	49.51	1.82
	sediment	4614.5	498.75	74.56	37.68	42.59	50.69	0.76
QH	*Tridacna maxima*	632.35	56.69	11.36	17.69	12.34	26.56	1.65
	sediment	8786.45	986.68	25.68	8.68	18.65	32.56	1.53
SH	*Tridacna maxima*	1286.38	65.21	29.78	26.83	35.32	38.26	1.79
	sediment	9546.34	1245.35	43.56	15.63	32.48	47.69	1.68
HH	*Tridacna maxima*	865.35	36.56	32.58	12.36	44.65	18.36	1.76
	sediment	3456.68	246.53	45.36	18.68	35.46	26.38	0.68
Eh	*Tridacna maxima*	421.02	36.52	29.45	37.02	39.54	48.21	1.63
	sediment	6897.36	169.36	36.25	82.69	34.65	42.36	1.32

HR=Hamata Reefs, Gh=Abu-Ghusun lagoon, WG=Wadi El-Gemal, QH=Quseir Harbor
SH=Safaga Harbor, HH=Hurghada Harbor, Eh=El-Esh area, *=values ppm

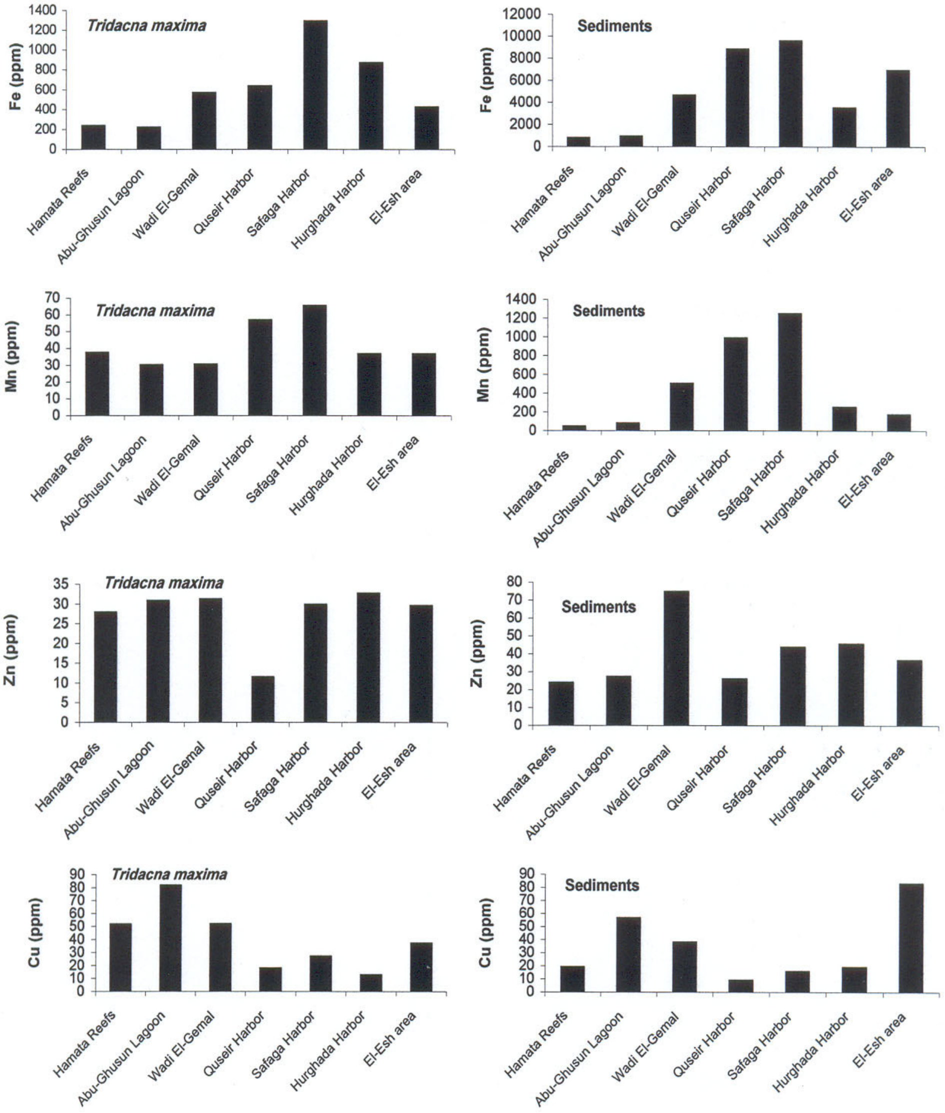

Fig. (3a). Heavy metal variations in the giant clam (*Tridacna maxima*) and sediments from the studied localities.

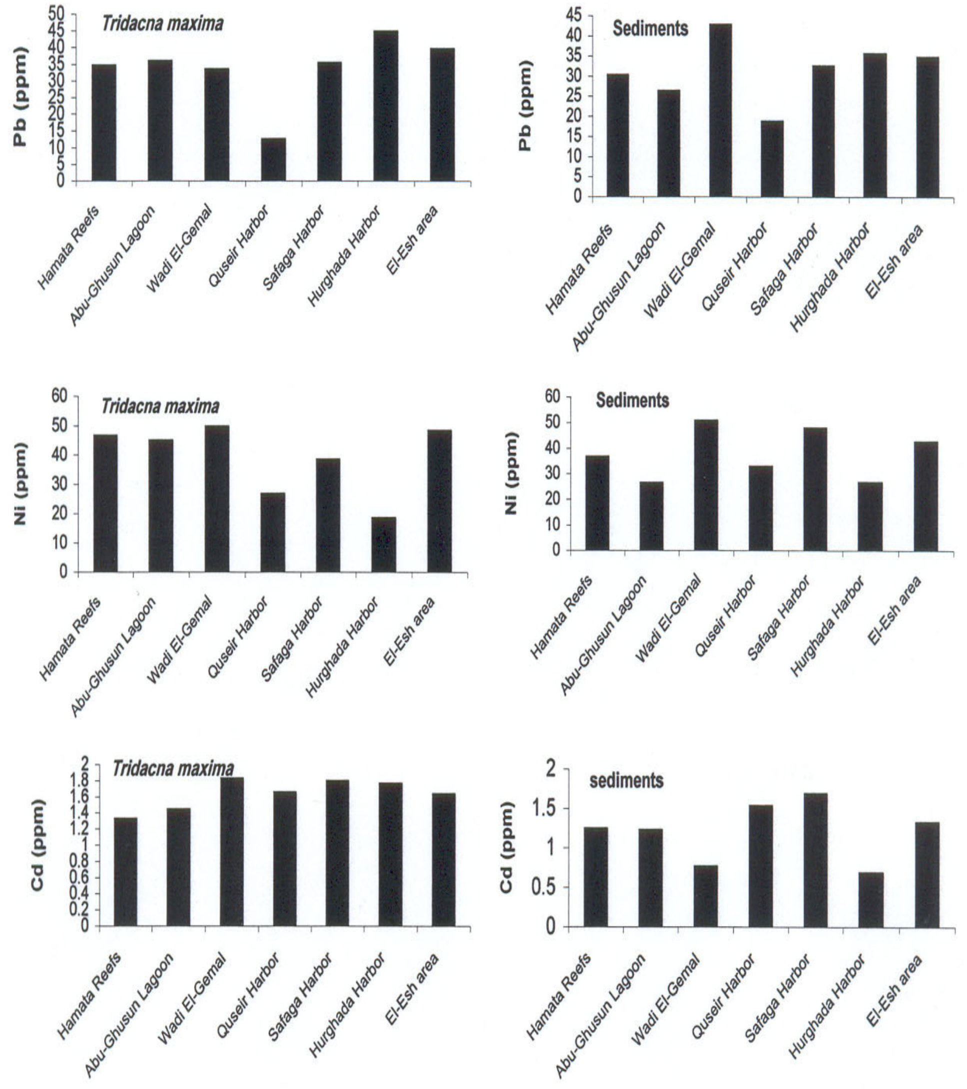

Fig. (3b). Heavy metal variations in the giant clam (*Tridacna maxima*) and sediments from the studied localities.

Lead and Nickel

Lead is leader member of the toxic metals in the marine environment. It is obvious that the Pb concentration in *Tridacna maxima* varies between 12.3ppm at Quseir Harbor and 44.7ppm at Hurghada Harbor. While in sediments, Pb ranges from 18.7ppm at Quseir Harbor to 42.6ppm at Wadi El-Gemal area (Fig. 3b). Similar to Cu, Pb content recorded high values in the shells of *Tridacna maxima* compared to the sediments except in Wadi El-Gemal and Quseir Harbor. Milliman (1974) showed that lead tends to be concentrated relative to calcium. He mentioned that lead within carbonates and most organisms accumulate over 100 times relative calcium. Generally, Pb in *Tridacna maxima* and the sediments attains high values at the anthropogenic sites except in Quseir Harbor. This is probably due to coal packing and other activities in Safaga Harbor. There are still some indications of coastal oil pollution observed around Hurghada Harbor. Oil production activities stopped some 20 years ago in Hurghada Harbor. Moreover, many safari boats and fishing ships using lead as sealing agent for ship bodies in the shipyards. Lead is mainly attributed to gasoline fuels containing high ratio of lead tetrachloride. In El-Esh area oil production and export activities provide kinds of pollution by hydrocarbons. On the other hand, the natural sites recorded high values of Pb contents relative to the shells of *Tridacna maxima* and the sediments. The main reason is attributed to the high contribution of terrigenous fragments by the wadis.

Ni content in the shells of *Tridacna maxima* changes from 18.4ppm at Hurghada Harbor to 49.5ppm at Wadi El-Gemal area, while in sediments, it ranges from 26.2ppm at Abu-Ghusun Lagoon to 50.7ppm at Wadi El-Gemal area (Fig. 3b). Nickel contents were higher in the shells of the giant clam compared to those of sediments in the natural impact sites. Mansour *et al.,* (2005) reported that the ability of invertebrates to adsorb metals is largely dependent on the physical and chemical characteristics of the metal as well as the seawater in which they live. Contrary to that result, Ni concentration in sediments is high compared to that of *Tridacna maxima* except in El-Esh area. Also, natural impact sites recorded high values of Ni contents in the shells of *Tridacna maxima* and the sediments. This indicates that the main source of nickel is the terrestrial sediments, either naturally by wadis in the natural sites or by human activities in anthropogenic sites. De Carlo and Spencer (1995) found that Ni and Co, do not display trends indicative of large anthropogenic contribution to the sediments.

Cadmium

Cd is not an essential element for plants, animals and human beings (Merian, 1991). The occurrence of cadmium in the marine environment is rare. Therefore, the impact of Cd on the environment is considerably small. The highest concentration of Cd in *Tridacna maxima* is recorded in Wadi El-Gemal area (1.82ppm), while the lowest one is in Hamata reefs (1.32ppm). On the other hand, Cd content in sediments ranges from 0.68ppm at Hurghada Harbor to 1.68ppm at Safaga Harbor (Fig. 3b). This means that the concentration of Cd in the shells of *Tridacna maxima* is 1.4 times that of sediments. Huanxin *et al.,* (2000) stated that cadmium is not needed for the giant clam growth and may even be deleterious. They suggested that Cd enrichment in shells is related to its similar geochemical properties to Ca, particularly ionic radius (cf. Ca 9.7 and Cd 9.8nm). Calcium has much higher abundance in seawater than Cd and is an essential element in the giant clam shell. Therefore, Cd probably enters the shell of *Tridacna maxima* as a substitute for Ca. The anthropogenic sites recorded the highest concentrations of Cd in the shells of the giant clam and sediments compared with those in the natural sites except in the sediments of Hurghada Harbor and in the shell in Wadi El-Gemal area. Cadmium sources in the anthropogenic sites come from phosphate shipment, ship traffic and coal packing especially in Safaga Harbor, tourist boats and oil seepage across pipelines in Hurghada Harbor, in addition to drilling fluids in oil fields at El-Esh area.

The results of comparison between heavy metal concentrations in the shells of the giant clam of the present work and the mollusc shells from other areas of the Egyptian coasts are shown in Table (3). Fe concentrations recorded high values in the anthropogenic sites of the present work compared to other studies of the Mediterranean Sea (Table 3). Also, Mn and Cu levels recorded high values compared to the former studies except in recent shells measured by Ziko *et al.,* (2001). Ramadan and Shata (1993), Okbah *et al.,* (1996), Shata and Hassan (2000) and Ziko *et al.,* (2001) recorded high concentrations of Zn and Pb in different molluscan shells from several areas compared with those in the shells of *Tridacna maxima* from the present studied localities (Table 3). On the contrary, Ni concentrations are high in the present work compared to the other studies of the Red Sea coast (Table 3). Cadmium concentrations recorded the lowest values in the shells of *Tridacna maxima* compared to their concentrations in other studies of the Egyptian Red Sea coast (Table 3).

This variation among molluscan shells of the studied localities and other studies of the Egyptian coast, indicates that bioaccumulation of heavy metals is species specific. This difference in spatial concentration for the different metals suggests that they are influenced by physical and chemical conditions from nature and human activity.

Cluster analysis (using Ward's method includes all measured metal concentrations Fe, Mn, Zn, Cu, Pb, Ni and Cd) in the shells of *Tridcana maxima* and the sediments from the studied localities were done. Three main clusters were distinguished (Fig. 4). Cluster 1 includes all samples of the giant clam of the studied localities and the sediment samples from Hamata reefs and Abu-Ghusun Lagoon. It is characterized by high concentrations of Cu (39.3ppm), Cd (1.554ppm) and Pb(32.4ppm). This cluster recorded the lowest values of Fe (652.9ppm), Mn (45.5ppm) and Zn (27ppm). This shows that the giant clam bioaccumulates some metals more than the associated sediments from suspended particles either as contaminated sediments or food particles. Therefore, heavy metal accumulations in *Tridacna maxima* are related to biogeochemical selectivity as well as to concentrations in water and sediments. Cluster 2 contains two sediment samples from Wadi El-Gemal and Hurghada Harbor, represent the highest concentrations of Zn (59.9ppm) and Pb (39ppm). Cluster 3 includes the sediment samples from Quseir, and Safaga Harbors and El-Esh area. It is characterized by high concentrations of Fe (8410ppm), Mn (800ppm), Ni (40.9ppm) and Cd (1.5ppm). The main source of pollution in Safaga and Quseir Harbors originates from the phosphate mining, shipping processes, cement and bauxite packing especially at Safaga Harbor.

Finally, metal variations are a result of both natural and human activity. Moreover, some molluscan species represent a valuable seafood source especially *Tridacna sp.* Therefore, high concentration of heavy metals in molluscan species give dangerous indicator to deteriorate the marine life and pose a health risk to humans.

Mechanisms of heavy metals accumulation in the giant clam

There are no relationships between the concentrations of heavy metals in shells of the giant clam and those in sediment (Fig. 5). This indicates that the heavy metals accumulated by *Tridacna maxima* are not directly derived from the sediment. Immega (1976) concluded, in his study of oyster shell, that many elements present in particles of "contaminated" inorganic detritus are incorporated into the shell at the mantle edge during formation. Sturesson (1976 & 1978) demonstrated that when Pb and Cd increased in the ambient seawater, they are incorporated into the shells at concentrations higher than normal. Therefore, there are two major sources of heavy metals in the shells of the giant clam. The first one is suspended particles, living or dead, and the second are

Table (3). Comparison of the heavy metal concentrations (ppm) in molluscan shells from the present work and other areas of the Egyptian coasts.

Location and type of recent mollusca	Heavy metals							Author
	Fe	Mn	Zn	Cu	Pb	Ni	Cd	
Port Said Mediterranean Sea (Bivalves shells) *Anadara diluvii*	100 - 309	12 - 50.01	69 - 325	25 - 54	130 - 160	~~~~	~~~~	Ramadan and Shata {1993}
Timsah Lake Suez Canal (Bivalves shells)	~~~~	~~~~	2.99 - 3.22	2.3 - 2.59	8.77 - 9.65	~~~~	1.93 - 2.14	Fikry {1995}
Lake Mariut sediments (Recent molluscan shells)	~~~~	~~~~	16 - 63	2 - 455	31 - 164	~~~~	3 - 17.0	Okbah et al., {1996}
Eastern Harbour of Alexandria (bivalves shells)	127 - 201.2	24.1 - 44.4	23.7 - 89.8	13.5 - 20.4	42.6 - 48.9	~~~~	~~~~	Shata and Hassan {2000}
Different areas of the Red Sea coast (Recent shells)	1152 - 3736	9 - 171	20 - 174	5 - 89.01	30 - 93	10 - 25.01	1.8 - 3.9	Ziko et al., {2001}
Different localities of the Red Sea coast (Molluscan shells)	524 - 1644	6.7 - 15.5	2.03 - 8.15	1.1 - 15.1	0.29 - 16.13	3.6 - 20	0.1 - 1.98	Madkour {2004}
Different localities of the Red Sea coast (*Tridacna maxima*)	216 - 1286	29.9 - 65.2	11.4 - 32.6	12.4 - 81.4	12.3 - 44.7	18.4 - 49.5	1.32 - 182	The present Work

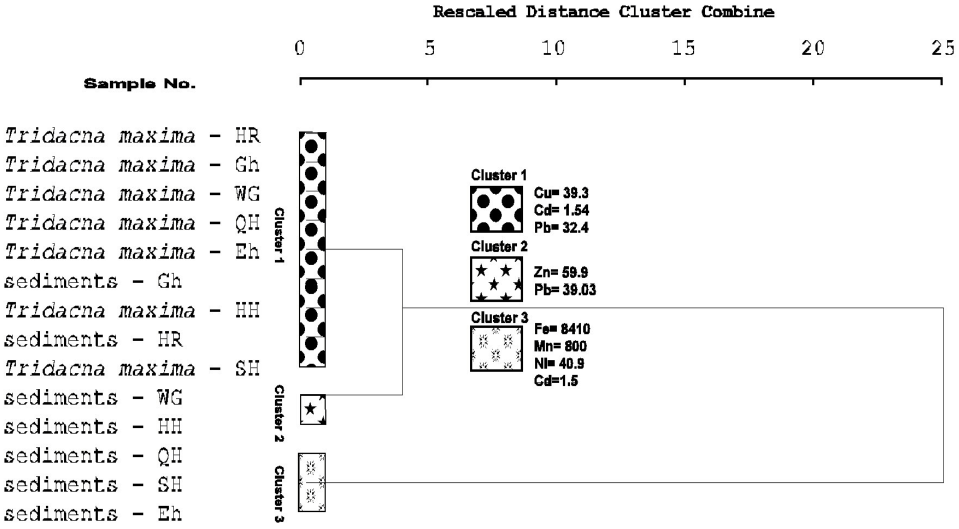

Fig.(4). Dedrogram from cluster analysis (ward's method) of heavy metals of *Tridacna maximma* shells and sediments throughout the studied localities.

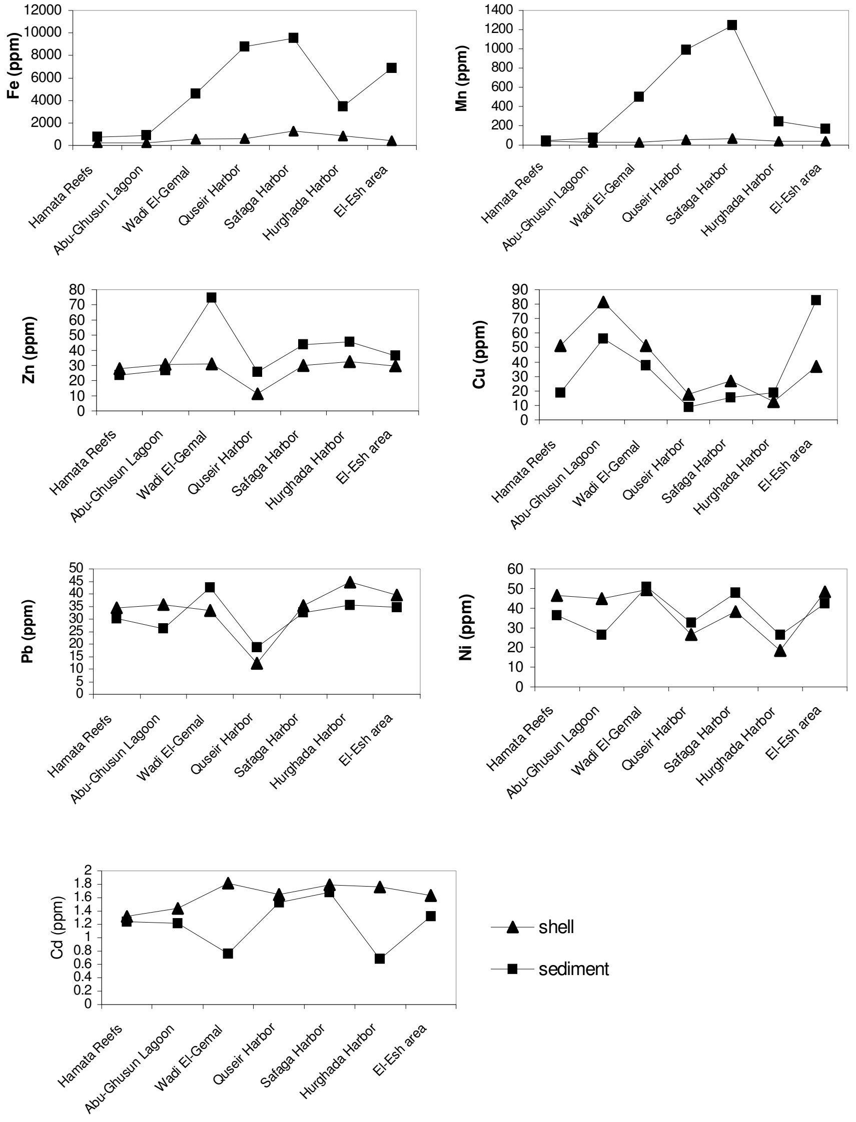

Fig. (5). Relation between concentrations of heavy metals in shells of *Tridacna maxima* and in sediments from the studied localities.

dissolved metals in the seawater, because *Tridacna maxima* is a filter feeder. It is very difficult to determine the relative importance of these two sources for any particular metal or location. Huanxin *et al.,* (2000) stated that in an environment affected by contaminant, both oyster tissue and shells have an opportunity to adsorb heavy metals from suspended particles. These suspended particles may be either as contaminated sediment or sediment controlled by the behavior of heavy metals themselves, and the physical and chemical conditions of the environment. Therefore, there are no clear relationships between concentrations of heavy metals in the giant clam shell and those in sediment.

CONCLUSIONS

Variability in heavy metal concentrations in *Tridacna maxima* could result from input of heavy metals from natural and human sources, environmental parameters and variations in the physiological condition of the giant clam.

Fe and Mn concentrations in sediments recorded high values than those in shells of *Tridacna Maxima* in all the studied localities especially in anthropogenic sites. Zn and Cu are enriched in the giant clam shells, which is related to their physiological function. The concentration of Pb in *Tridacna maxima* is high than that in sediments in most studied localities especially in anthropogenic sites. On the other hand, Ni content in *Tridacna maxima* have high values in the natural impact sites compared with that in anthropogenic sites. Cadmium is enriched in *Tridacna maxima* relative to sediments in the studied localities especially in anthropogenic sites because of the easy substitution between Cd and Ca. Therefore, heavy metals accumulation in *Tridacna maxima* is related to biogeochemical features and the giant clam's physiology as well as to concentrations in seawater and sediments.

This study shows that, there are no clear relationships between concentration of heavy metals in the shells of *Tridacna maxima* and those in sediments. Finally, the concentration of heavy metals in the giant clam shells and in sediments has considerable spatial variability in the studied localities.

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